10TH TRENDS IN BREWING
Ghent, Belgium. April 1st-5th 2012

Fingerprinting of hop oil constituents and sensory evaluation of the essential oil of hop pellets from pure hop varieties and single-hop beers derived thereof

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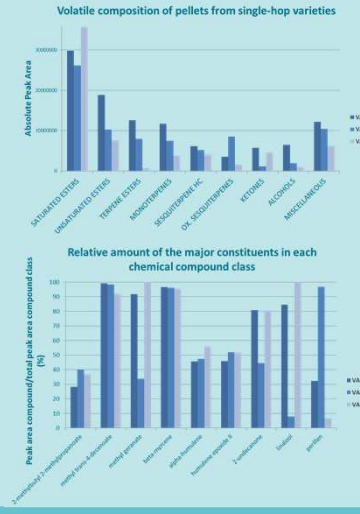
INTRODUCTION

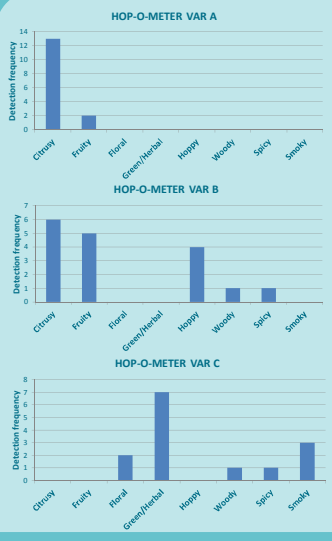
Hops impart both bitterness and hoppy aroma to beer. In respect of hoppy aroma, late- and dry-hopping techniques are applied to prepare beers with a pronounced, varietal dependent hop aromatic character. The characteristic hoppy odour/aroma of the final beer prepared via late- and dry-hopping is mainly determined by the hop variety used and is caused by the volatiles originally present in, or derived from, hop essential oil. In this study, we aimed at analytical and sensory characterisation of pellets from three distinctly different commercial hop varieties and six single-hop beers aromatised with these particular varieties. For each hop variety, two beers, i.e. late-hopped beer with and without an additional dry-hopping step, were brewed on a 40 hL scale. The presented results are part of a research project of which the main objectives are (1) to find sensory and analytical correlations between hops as raw material and the beers derived thereof, (2) accurate analytical measurement of hoppy aroma of beer, (3) determination of flavour-impact compounds for hop aroma and hoppy aroma of beer, and (4) study of the stability of hoppy aroma.

ANALYTICAL AND SENSORY ASSESSMENT OF HOP AROMA

ANALYTICAL FINGERPRINTING



- The volatile composition of pellets from three single-hop varieties (VAR A, VAR B, VAR C) was investigated via headspace solid-phase microextraction **(HS-SPME)** and gas chromatography-mass spectrometry **(GC-MS)**.
- More than 100 volatiles were detected and classified into several chemical compound classes.
- The **hop varieties** are clearly **differentiated** based on the **composition and level of each chemical compound class.**
- The relative amount of the most abundant volatile in each chemical compound class is graphically displayed showing **clear differences in composition of saturated esters, terpene esters, ketones, and alcohols** between the hop varieties investigated.

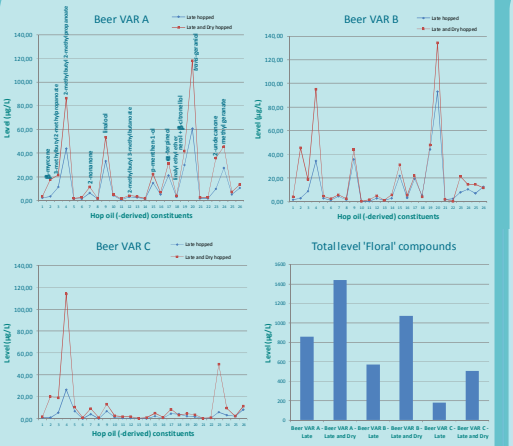


SENSORY PROFILES

- For sensory evaluations of hop aroma, the total essential oils of three hop varieties (VAR A, VAR B, VAR C) were selectively isolated from the hop pellets by supercritical fluid extraction using carbon dioxide.
- By adding appropriate amounts of the total essential oils to model solutions (ethanol-water, 5% v/v), the sensory properties were investigated and, as a result, **characteristic 'hop-o-meters'** reflecting the typical odour/aroma of each hop variety were established.
- Striking differences between the varietal hop oils were observed in respect of the descriptors 'Citrus' (grapefruit) - VAR A; 'Fruity/Citrus (orange)' and 'Hoppy' - VAR B; 'Green/Herbal' and 'Smoky' - VAR C.

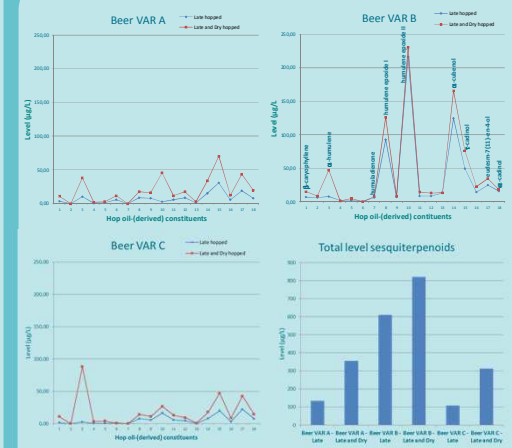
ANALYTICAL AND SENSORY ASSESSMENT OF HOPPY AROMA OF LATE- AND DRY-HOPPED BEERS

'FLORAL'-COMPOUND FINGERPRINTS



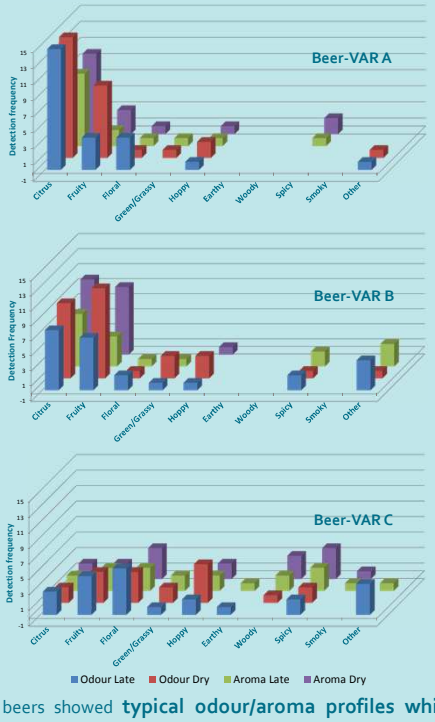
- The volatile composition of the beers, late- and dry-hopped with VAR A, VAR B or VAR C was determined via HS-SPME and GC-MS. **Extracted ion chromatograms** (m/z=58, 69, 71, 72, 74, 93, 136) were generated to detect hop oil (-derived) **monoterpenes and oxygenated compounds** ('Floral'-compounds).
- Based on the detection of 26 hop oil constituents originally present in hop essential oil (e.g. β-myrcene, linalool, geraniol, 2-undecanone, methyl geranate) and hop oil-derived constituents (e.g. α-terpineol, terpinyl ethyl ether) **characteristic analytical fingerprints** are obtained for each of the single-hopped beers investigated.
- Next to varietal differences between the beers, **differences between late- and dry-hopped beers brewed with the same variety** are observed.
- Dry-hopping increases the total level of floral compounds (1.7 (VAR A) – 2.8 (VAR C) times).

SESQUITERPENOID FINGERPRINTS



- The volatile composition of late- and dry-hopped beers was determined via HS-SPME and GC-MS. **Extracted ion chromatograms** (m/z= 69, 93, 109, 138, 161, 189, 204, 220, 222) were generated to detect hop oil-(derived) **sesquiterpenoids**.
- Based on the the detection of 18 hop oil constituents originally present in hop essential oil (e.g. β-caryophyllene, α-humulene, humulene epoxides) and hop oil-derived constituents (e.g. caryophyllenyl alcohol, humulol) **characteristic analytical fingerprints** are obtained for each of the single hopped beers investigated.
- The beers brewed with VAR B contained significantly higher levels of humulene epoxides. Higher levels of the oxygenated sesquiterpenes differentiated pellets of hop variety B from the other varieties.
- Dry-hopping increases the sesquiterpenoid level of the beers.

SENSORY PROFILES



All beers showed **typical odour/aroma profiles which reflect the sensory characteristics of the hop essential oils**. Beers hopped with VAR A or VAR B have pleasant and pronounced citrus (grapefruit) or citrus (orange)/fruity scents, respectively. The hoppy aromatic character of beers brewed with VAR C was less pronounced in terms of 'citrus' or fruity and was described using many descriptors (floral, hoppy, spicy, green/herbal, woody).

CONCLUSION

Characteristic analytical and sensory fingerprints of hop pellets from three distinctly different commercial hop varieties were obtained via HS SPME GC-MS and 'hop-o-meters' resulting from sensory evaluations of hop essential oil in model solutions. Analytical fingerprints of hop oil-derived constituents in the fresh beers show (1) significant differences between late- and dry-hopped beers brewed with the same hop variety, and (2) varietal differences between both late- and dry-hopped beers. The sensory properties of the varietal hop oils are clearly reflected in the resulting single-hop beers and, although further investigation is required, the presented data also point to a relationship between the analytical hop oil-derived profiles in the beers and the sensory perceptions of varietal hoppy aroma.

Acknowledgement: we would like to thank IWT Vlaanderen for financial support